THE CONTENTS OF THIS SECTION ARE
THE HIGHEST QUALITY AVAILABLE

INITIAL _MO_ DATE _9/27/01_

APPENDIX G

Plutonium and Uranium Modeling Data

ACTINIDE MOBILITY AT THE SOIL CONSOLIDATION UNIT

Jonathan Myers, International Technology Corporation, Albuquerque, New Mexico, **James D. Navratil**, Lockheed Martin Idaho Technologies Company, Idaho Falls, Idaho

7/17/98 Draft

The migration behavior of actinides (such as plutonium and uranium) in the subsurface at the Idaho Nuclear Technology and Engineering Center (INTEC), formally the Idaho Chemical Processing Plant (ICPP), is not well understood. This information deficiency prevents the accurate prediction of potential impacts of actinides in the planned Soil Consolidation Unit (SCU) at the INTEC. More rigorous estimates of distribution coefficient (K_d) values for soil/solution pairings in the sedimentary interbed and potential SCU liner materials, as well as contaminated soils at the INTEC, are needed to support accurate cleanup decisions and to develop a realistic Waste Acceptance Criteria for the SCU.

The potential for plutonium to leach from the Tank Farm Soils (TFS) must also be evaluated. If the leachable concentration of plutonium is lower than the maximum concentration limit (MCL) allowed for plutonium, then the Kd is of much less importance since the MCL would not be exceeded in the aquifer in any case. However, the current TFS inventory represents over 90% of the plutonium source for potential transport through the vadose zone. The current groundwater modeling approach assumes a K_d for plutonium of 22 in interbed sediments between the TFS (source) and the aquifer. The resulting calculated risk values are above 1 in 10,000 excess cancer risk for exposure to plutonium when the peak modeled concentration occurs (Rodriguez, et al., 1997).

This brief summary and interpretation report is based on existing data and will present the current state of knowledge of plutonium and uranium mobility issues for the TFS. The data review includes a description of waste processes generating the actinides in the TFS, summary of available soil characterization data, evaluation of the ability of the TFS to sorb actinides for the applicable range of solution chemistries, and the effect of co-releases on the mobility and chemical forms of actinides released from the TFS.

Actinide Generating Waste Processes

The INTEC has been in operation since 1954 and has historically been a uranium reprocessing facility for defense projects and for research and storage of spent nuclear fuel. After fuel dissolution and extraction, several types of high-level radioactive liquid wastes have been produced. In the past inadvertent releases of radioactivity have contaminated some of the subsurface at the INTEC.

The R,1TEC fuel dissolution processes produced a solution of uranyl nitrate for several cycles of solvent extraction processing. The purposes of the solvent extraction processes were to separate the uranium from the residual fission products and transuranic elements, recover most of the uranium as product, and after reducing its volume, transfer the waste material to storage. The first-cycle solvent extraction process preferentially separated uranium from fission products using tributyl phosphate (TBP) in a hydrocarbon diluent, whereas subsequent extraction cycles separated the transuranics. The second- and third-cycle extraction processes used methyl isobutyl ketone to purify the uranium product from the first-cycle extraction.

Following reprocessing, the wastes were directed to the high-level liquid waste (HLLW) Tank Farm or process equipment waste (PEW) Evaporator Facility. Table 1 summarizes the estimates

of volume, duration, and quantity of radioactivity released at each of the three tank farm sites as well as the other two known or estimated release sites. Chemical components in the first two releases will be highlighted below since they account for the majority of the activity released.

The majority of liquid waste stored in the Tank Farm was generated during the first-, second, and third-cycle extraction processes. These raffinates include high-level wastes that are composed of first- and second-cycle raffinates and intermediate-level wastes that are composed of third-cycle raffinates blended with concentrated bottoms from the PEW Evaporator. Additional wastes stored in the Tank Farm include fluoride and cadmium bearing wastes from the fluorinel process, decontamination wastes containing fluoride from waste calcining and other process salvage streams (Rodriguez, et al., 1997).

The release identified with CPP-28 and CPP-79 is assumed to be first cycle waste; therefore, radionuclide estimates relied exclusively on data from the analysis of first cycle waste (Rodriguez, et al., 1997). The data of Rhodes (1972) provides the results of non-radioactive chemical analyses of
first cycle waste samples obtained from the tank farm in September 1971. These data are shown in Table 2. Table 3 provides average non-radioactive chemical composition of tank farm waste for estimating constituents in CPP-31 (Donovan, 1989). Rodriguez, et al., (1997) provides the maximum, minimum, and average value of the total mass release estimates for nonradioactive constituents from CPP-28, CPP-79 and CPP-31. These data were used to formulate the information in the last two sections of this report.

Available Soil Characterization Data

There has been some sampling of the TFS, but the analysis performed was mainly for radiological content of the soils. No actinide speciation data are available. The available information on chemical contamination in the soils is shown in Table 4. Additional descriptive information on CPP-28, -79 and -31 follows.

In 1974, soil with radioactive contamination up to 40 R/hr was encountered at a depth of about 1. 8-m (6 ft) below ground surface (bgs) at CPP-28. The leak was later determined to be from a hole inadvertently drilled through one side of a pipe during original construction in 1955. HLLW consisting of first-cycle raffinate most likely leaked through secondary containment to the surrounding soil and may have occurred as early as 1955 (Rodriguez, et al., 1997).

Six soil borings were drilled on October 10, 1994, and one soil sample was collected from the bottom of a borehole. The depth of sample collection for the beta-gamma radiation measurements ranged from 2.0 to 3.0 m (6.5 to 10 ft) bgs. Only one soil sample indicated radiological contamination at a level of 40 R/hr beta-gamma on contact. Isotopic analyses were not performed on any of the soil samples. It is now believed that most of these boreholes were not drilled deep enough to intercept soil contamination.

No sampling data are available to accurately delineate the extent of contaminated soil in the vicinity of site CPP-28. Contaminants have likely migrated further to the south than to the north due to the presence of a tank immediately north of site CPP-28. It is also possible, if not likely, that preferential migration pathways may be present in the form of sandy backfill commonly

placed in pipeline excavations. Considering the high radiation levels on the 9. I-m (30-ft) sample, it is also likely that contamination extends downward to the soil/basalt interface at a depth of about 12.8 (42 ft).

CPP-79 was originally defined as soil contaminated by the releases of waste solutions in July and August of 1986 due to an obstruction in a transfer fine. A second, deeper zone of contamination at this site is believed to be related to the release of HLLW at site CPP-28. During a CPP-79 investigation, one soil boring was drilled in the alluvium near the release to determine the type and concentration of the residual contamination and to characterize the deeper soils in the Tank Farm area. A total of 15 split-spoon samples were collected from the borehole. The split-spoon samples were screened in the field for gross beta-gamma radiation and a total of seven samples were selected from the zones having the highest radiation for further analysis. Samples were analyzed for VOCs, mercury, cadmium, nitrate/nitrite, pH, and radionuclides. These results are summarized on Table 4.

An investigation of the source of contamination at site CPP-31 revealed that in November 1972 HLLW was released to the surrounding soil during a transfer between two tanks. The release was caused by a failure of a waste transfer line where it was speculated that the highly acidic BLLW corroded the transfer line, located about 2 ft bgs. Soil sample data are not available to delineate the extent of chemical contamination.

Chemical Forms and Mobility of Actinides Released from TFS

The solubility and speciation of plutonium and uranium in INEEL groundwater was calculated using version 7.2b of the EQ3NR code (Wolery, 1992) along with version 8 release 6 of the "composite" thermodynamic database compiled by Lawrence Livermore National Laboratory. This version of the database contains a total of 80 elements, 1768 aqueous species, 93 gases, and 1130 solid phases. The 31 aqueous plutonium species and 11 solid plutonium-bearing phases that are part of the database are listed in Table 5. Table 6 shows the 79 aqueous uranium species considered in the model.

Two groundwater compositions were used in the model. A high fluoride composition is based on a synthetic INEEL perched groundwater formulation provided in Fjeld et at, 1998; and a low fluoride composition is based on analyses of perched groundwater samples collected near the Chemical Processing Plant (Rodriguez, et al., 1997). The compositions of these two formulations are provided in Table 7. The effects of pH were assessed by using a pH of 8, which is the undisturbed groundwater value, and a pH of 6, which may represent groundwater impacted by tank farm waste. Modeling results indicate that both groundwaters are in equilibrium with calcite ($CaCO_3$) at a pH of 8, and are undersaturated with respect to calcite at an assumed pH of 6. The high fluoride groundwater is in equilibrium with fluorite (CaF_2) at both pH values. The redox state of the groundwater is a key parameter affecting plutonium solubility and speciation but is poorly characterized. The redox was varied in the calculations over a range of redox potentials to assess the effects of this parameter in both the high-fluoride and low-fluoride groundwaters. The concentrations of plutonium and uranium were controlled by assuming equilibrium with an appropriate stable solid phase.

The effect of other ligands originally present in the waste solutions, such as TBP and its hydrolysis products, and naturally occurring organics, such as humic acids, were not considered in the calculations. These ligands are assumed to play a lesser role in transport as compared to hydrolysis reactions and colloid formation.

Plutonium-Solubility and Speciation The predicted solubility of plutonium for three cases (low F⁻ at pH 8, high F⁻ at pH 8, and high F⁻ at pH 6) is shown as a function of redox potential (+200 to +700 mV) in Table 8 and Figure 1. $Pu(OH)_4$ was the predicted stable phase at pH 6 over the 200 to 700 mV redox range considered. At pH 8, $PU(OH)_4$ was the predicted stable phase below a redox potential 630 mV and $PUO_2(OH)_2$ was predicted above a redox potential of 630 mV. Results for all three cases show a marked increase in solubility above a redox potential of 500 mV, corresponding to the oxidation of Pu IV species to the more soluble Pu V and Pu VI species. The low fluoride composition shows lower solubilities than the other groundwater compositions under oxidizing conditions because of the absence of fluoride species. The solubility under oxidizing conditions is limited above a redox potential of 630 mV by the precipitation of $PUO_2(OH)_2$, which controls the solubility at 2×10^{-7} M.

In the high fluoride groundwater at a pH of 8, the solubility above 630 mV is also limited by the precipitation of $PUO_2(OH)_2$. A pH of 6 is too low for the precipitation of $PuO_2(OH)_2$ so the solubility continues to rise above 630 mV under the control of PU $(OH)_4$. At redox potentials below 300 mV, the solubility at pH 8 remains quite low ($\sim 2 \times 10^{-9}$ M). However, at pH 6, Pu III species $(Pu^{+3}, PuSO_4+$, and $Pu(SO_4)_2^-)$ become stable and contribute to increasing solubility.

The speciation of plutonium in the low fluoride pH 8 composition is shown in Table 9 and Figure 2; the high fluoride pH 8 composition is shown in Table 10 and Figure 3; and the high fluoride pH 6 composition is shown in Table 11 and Figure 4. The species shown contribute >99 percent of the total solubility. The complexity of plutonium speciation is evident in these results. At redox potentials above 500 mV, which is a likely condition in the vadose zone, between three and five different species are present at significant percentages of the total dissolved plutonium.

These species have a variety of different charges, including -2, -1, 0, and +1. Under oxidizing conditions, anionic fluoride species $[PuO_2F_4^{-2}$ and $PUO_2F3^-]$ dominate in the high fluoride compositions, and the anionic carbonate form $[PUO_2(CO_3)_2^{-2}]$ dominates in the low fluoride composition. Under reducing conditions, the neutral $Pu(OH)_4$ form dominates, but at pH 6, the Pu III species become increasingly significant as the redox potential drops below 300 MV.

Uranium Solubility and Speciation The predicted solubility of uranium in two groundwaters (low F⁻ at pH 8 and low F⁻ at pH 6) is shown as a function of redox potential (-300 to +650 mV at pH 8, and -200 to +800 mV at pH 6) in Table 12 and Figure 5. At a pH of 8, calcium uranate $(CaUO_4)$ is the stable phase above +50 mV and uraninite (UO_2) is the stable phase below +50 mV. At a pH of 6, uranyl carbonate (UO_2CO_3) is the stable phase above +150 mV and uraninite is the stable phase below +150 mV.

Results for both cases (low F- at pH 8 and low F_ at *pH 6)* show low solubilities in the range of *5x10-10* M below a redox potential of ~0 mV, with a marked increase to IxIO-4 M above -150 mV. This increase in solubility of almost six orders of magnitude corresponds to the oxidation of U (IV) species to the more soluble U (VI) species as well as a shift in the controlling phase from

the tetravalent uraninite *to* the hexavalent CaU04 (PH 6) or UO_2CO_3 (pH 8) as the redox potential increases.

The speciation of uranium in the low F⁻ groundwater at a pH of 8 is shown in Table 13 and Figure 6, and the speciation in the low F- groundwater at a pH of 6 is shown in Table 14 and Figure 7. The species shown contribute to >99 percent of the total solubility. Under reducing conditions (below -100 mV at pH 8, and below +100 mV at pH 6), the speciation is dominated by the neutral tetravalent $U(OH)_4$ form. Under oxidizing conditions, a mixture of hexavalent uranyl carbonate, hydroxy, and mixed carbonate-hydroxy species are dominant. At pH 8 above -100 mV, the speciation is dominated by $UO_2(CO_3)_3{}^{-4}$, $UO_2(CO_3)_2{}^{-2}$, and $(UO_2)_2CO_3(OH)_3{}^{-}$ in that order. At pH 6 above +100 mV, the speciation is dominated by $UO_2(CO_3)_2{}^{-2}$, $(UO_2)_2CO_3(OH)_3{}^{-}$, $UO_2CO_3(aq)$, $UO_2(OH)_2(aq)$, UO_2OH^{+}, and $UO_2(CO_3)_3{}^{-4}$ in that order. The difference in uranium speciation at pH 8 versus pH 6 is indirectly caused by carbonate speciation. At pH 6, most of the total dissolved carbon is in the form of $HCO_3{}^{-}$ which is a form that is unavailable for uranium complexation. At higher pH condition, a greater proportion of total dissolved carbon is in the form of $CO_3{}^{-2}$, which is a strong uranium complexing ligand.

Ability of TFS to Sorb Actinides

Adsorption of dissolved groundwater constituents along flow paths is a complex process that can be subject to a large number of site-specific variables. There are however, a few generalizations that can be drawn from the speciation results. At neutral pH clay minerals have a net negative surface charge, and iron- and manganese-oxides have a net positive surface charge. Because of these surface charges, cationic (positively charged) species tend to adsorb on clay minerals; anionic (negatively charged) species tend to adsorb on iron- and manganese-oxide minerals; and neutral species tend to display little or no adsorption (Drever, 1982). The higher the charge on the species, the stronger the attraction on mineral surfaces with opposite charge, and the stronger the repulsion on mineral surfaces with the same charge.

The soils in the vicinity of the tank farm are dominantly composed of silt (13 to 88%) and sand (S to 85%), with lesser amounts of clay (2 to 15%) (INEL, 1994). This type of soil is predicted to provide fairly good adsorption of cationic species, but poor adsorption of anionic or neutral species. The percentage of plutonium existing as cationic species is at a maximum of 30 to 70 percent (depending on the composition) at a redox potential of -550 mV, but the percentage of cationic species is much less at both higher and lower redox potentials. For instance, the speciation of plutonium at 700 mV and a pH of 8 in the high fluoride groundwater is $PUO_2F_4{}^{-2}$ (46%), $PuO_2F_3{}^{-}$ (45%), and $PUO_2(CO_3)_2{}^{-2}$ (9%). The uranium speciation is likewise dominated by anionic species under oxidizing conditions, and neutral species under reducing conditions. These dominant plutonium and uranium species would not be expected to adsorb very strongly on silty tank farm soils.

Modeling the transport of uranium or plutonium when the*y* are present as several different species with different charges presents a problem. The use of a single K_d is an oversimplification because each of the species will migrate at different velocities. The situation is compounded by the fact that in a system at equilibrium, the ratios between all of the species of a given element are fixed. The selective adsorption of one or more species will create disequilibrium in the aqueous phase as

it migrates along the flow path. The system will respond by re-apportioning the remaining dissolved

element between the stable species in an attempt to re-establish the equilibrium ratios. The rate at which the transformations between species occur varies. Transformations involving changes in the plutonium or uranium valence state occur more slowly than simple transformations such as $PuO]F_3^- + F^- \Leftrightarrow PuO_2F_4^{-2}$, or $UO_2CO_3(aq) + CO_3^{-2} \Leftrightarrow UO_2(CO_3)_2^{-2}$. Adsorption and desorption processes simultaneously occur at different rates, and the groundwater moves at some rate. The relative differences between rates of species transformation, adsorption, desorption, and groundwater flow, control the extent to which chemical equilibrium is maintained in the water-sediment system.

The use of a weighted average K_d may accurately describe the transport of the central portion of the plume, but it may seriously underestimate the velocity of the leading edge of the plume. The use of a conservative (low) K_d based on the most mobile form may accurately describe the leading edge of the plume, but the concentrations at the leading edge may be insignificant. An alternative approach is to apportion the total dissolved plutonium among the major species and assigning a different K_d to each one. These species can then be treated as separate constituents in a transport model, and then summed to predict concentration (or dose) versus time at a receptor site. Transformations between the species would be difficult to account for in such a model, and may introduce large uncertainties in the results.

The use of empirical break-through curves from column sorption experiments on native soils can provide insight into actinide mobility and can validate speciation modeling results. Differences in the transport properties of each of the major species that are present will show up as inflections in the cumulative break-through curve. The experiments can be scaled so that the water velocities are in the same range as the actual conditions, or alternatively, can be performed at several higher velocities and the results extrapolated to the actual conditions. These experiments, coupled with solubility-speciation modeling, provide the best approach to estimating actinide mobility.

References

Donovan, R. I., 1989, Tank Farm Inventory, Westinghouse Idaho Nuclear Company, Inc., Letter and Attachment to A. P. Hoskins: RID-08-89, August 14,1989.

Drever, J. 1., 1982, The Geochemistry of Natural Waters, Prentice-Hall Inc.

Fjeld, R. A., 1998,J. T. Coats; W. W. Elzerman and J.D. Navratil, "Column Studies of Plutonium Transport in Sedimentary Interbed From the Snake River Plain," Proceedings of WM'98, 38-08.

INEL, 1994, "Technical Memorandum on the Hydrogeology at the Idaho Chemical Processing Plant", Lockheed Idaho Technologies Company, Idaho National Engineering Laboratory, Idaho Falls, Idaho.

Rhodes, D. W., 1972, Composition of First- and Second-Cycle Wastes, Allied Chemical Corp. Interoffice Correspondence: Rhod-4-72, August 7, 1972.

Rodriguez, et al., 1997, Comprehensive RI/FS for the ICCP OU 3-13 at the INEEL-Part A, RI/BRA Report, DOE/ID-10534, November 1997.

Wolery, T. J., 1992, EQ3NR, "A Computer Program for Geochemical Aqueous Speciation-Solubility Calculations: Theoretical Manual, Users Guide, and Related Documentation (Version 7. 0)", Lawrence Livermore National Laboratory, UCRL-MA- 110662 PT III.

Table 1 Release estimate summary for liquid release sites in the vadose zone.

Release Name	Release[a] Volume	Release[b] Duration	Begin[b] Date	End[b] Date	Estimate of Total Activity Released
	(1)	(days)			(Ci)
CPP-28/79	13,736	6,84	1/1/56	10/1/74	32,661
CPP-31	52,990	2	11/1/72	11/30/72	28,000
1986	9,508	2	7/7/86	8/2/86	43
CPP-02	181,074,400	4,74	1/1/54	12/31/66	493
CPP-80	399,318	2,55	1/1/83	12/31/89	550

[a]Release volume for CPP-28/79 is determined by bounding calculations an the maximum throughput of a 1/8" diameter hole in a transfer line assuming a total volume Of 1.234×10^{-7}L (3.26×10^6 gal) passed through the line under a pressure of 1.83 m(6ft) see Appendix; the release volume for CPP-31 is provided in Allied Chemical Corp.(1975); the release volume for the 1986 is provided in WINCO (1986); the release volume for CPP-02 is provided in USGS (1974); the release volume for CPP-80 is provided in WINCO (1993).

[b] The release duration and dates for CPP-28/79 are estimated by assuming the release occurred from the time of construction (approximately 1/1/56) until time of Discovery of the release (10/1/74); release duration and dates for CPP-31 are provided in Allied Chemical Corp. (1975); the release duration and dates for the 1986 are provided in WINCO (1986); the release duration and dates for CPP-02 are provided in USGS (1974); the release duration and dates for CPP-80 am provided in WINCO 1993).

[c]The total activity release estimate for CPP-28/79 is determined using a release volume of 13,736 L (3,629 gal) with an activity concentration of 2.38 Ci/L (9 Ci/gal); activity release estimate for CPP-31 is provided in Allied Chemical Corp. (1975); the total activity release estimate for the 1936 is determined using a maximum process equipment waste (PEW) activity concentration of 1×10^7 d/min/ml (0.017Ci/gal) and a release volume of 9508 L(2512 gal); the total activity release estimate for CPP-02 is provided in USGS (1974); the total activity release estimate for CPP-80 is provided in WINCO (1993).

Table 2 Non-radioactive chemical constituents of first cycle waste -From Rhodes (1972)

Non-radionuclide	WM-185	WM-187	WM-198	Units
H+	1.5	1.62	1.72	M
Al+3	0.6	0.64	0.69	M
Zr+4	0.4	0.44	0.48	M
F-	3.1	3	3.52	M
B	2.1	2.08	2.34	g/L
N03-	2.3	2.32	2.4	M
Fe+3	0.25	0.225	0.298	g/L
Cl-		12	37	mg/L
Na	2	60	74	mg/L
H+	1.522E-0	1.633E-03	1.734E-03	kg/L
Al+3	1.835E-0	1.727E-02	1.862E-02	kg/L
Zr+4	4.014E-0	4.014E-02	4.379E-02	kg/L
F-	5.928E-0	5.700E-02	6.687E-02	kg/L
B	2.160E-0	2.080E-03	2.340E-03	kg/L
N03-	1.463E-0	1.439E-01	1.488E-01	kg/L
Fe+3	2.570E-0	2.250E-04	2.980E-04	kg/L
Cl-	9.000E-0	1.200E-05	3.700E-05	kg/L
Na	2.900E-0	6.000E-0	7.400E-05	kg/L

Table 3 Non-radioactive chemical constituents of tank- farm waste from Donovan (1989).

Nonradionuclide	WM-180	WM-181	WM-182	WM-183	WM-184	WM-185	WM-186	WM-187	WM-188	WM-189	Units
H+	1.92	1.51	0.83	1.71	0.43	1.71	1.4	1.51	1.79	1.8	Normal
NO3	5.79	3.24	4.11	4.5	4.63	5.05	2.93	1.39	1.78	2.28	M
Al	0.55	0.21	1.19	0.5	0.81	0.71	0.35	0.43	0.29	0.18	M
Na	1.78	0.83	0.02	0.7	1.98	1.38	0.96	0.02	0.03	0.05	M
K	0.23	0.12		0.1	0.13	0.18	0.16		0.01	0.04	M
F	0.05	0.08	0.07	0.0	0.04	0.15	0.04	2.32	1.74	0.28	M
Zr		0.01	0.01			0.01		0.31	0.26	0.03	M
B	0.26	0.17	0.13	0.1	0.08	0.29	0.22	1.62	1.81	0.26	g/L
Cd	0.17	0.49	0.20	0.1	0.02	0.10	0.19	5.82	11.59	1.22	g/L
Ca		1.78		1.5	0.44	2.55	2.52			4.35	g/L
Cl	0.74	0.27	0.05	0.2	1.54	1.08	0.7	0.05	0.05	0.12	g/L
Cr		0.13		0.6	0.11	0.28				0.09	g/L
Fe	1.41	0.66	1.14	3.0	1.11	1.22	1.01	0.3	0.37	0.25	g/L
Pb		0.21		0.2	0.20	0.17					g/L
Hg		0.10		0.5	0.31	0.86					g/L
Mo		0.05		0.0	0.05	0.05				0.05	g/L
Mn		0.71		0.7	0.46	1.05.16					g/L
Ni		0.07		0.3	0.07	0.10				0.05	g/L
P		O.19		0.1	0.73	0.08					g/L
SO$_4$	2.97	3.85	4.18	0.81	6.66	3.73	3.2	3.49	6.59	0.86	g/L

Table 4 Available Data on Chemical Contaminants in Soil Samples

Table 5 Plutonium-bearing aqueous species and solid phases considered in model

Aqueous Species

Bare cation	Pu^{+4}	
Oxy	PuO_2^+	PuO_2^{+2}
Hydroxy	$Pu(OH)_2^{++}$ $Pu(OH)_4(aq)$ $PuO_2OH(aq)$ $PuOH^{+2}$	$Pu(OH)_3^+$ $PuOH^{+3}$ PuO_2H^+
Phosphates	$Pu(HPO_4)_2(aq)$ $Pu(HPO_4)_4^{-4}$ $PuHPO_4$	$Pu(HPO_4)_3^{-2}$ $PuH_2PO_4^{+2}$ $PuO_2H_2PO_4^+$
Sulfates	$Pu(SO_4)_2(aq)$ $PuSO_4$ $PuO_2SO_4(aq)$	$Pu(SO_4)_2^-$ $PuSO_4$
Fluorides	PuF^{+3} PuF^{+3} PuO_2F^+ $PuO_2F_3^-$	PuF_2^{+2} $PuF_4(aq)$ $PuO_2F_2(aq)$ $PuO_2F_4^{-2}$
Carbonates	$PuO_2(CO_3)_2^{-2}$	
Chlorides	PuO_2Cl^+	

Solid Phases

	Plutonium $Pu(HPO_4)_2$ $Pu(OH)_4$ PuF_3 PuO_2 PuO_2HPO_4	$Pu(OH)_3$ Pu_2O_3 PuF_4 $PuO_2(OH)_2$ $PuO_2OH(am)$

Table 6 Uranium-bearing aqueous species considered in the model

Bare cation	U^{+3}	U^{+4}		
Oxy	UO_{2+}	UO_{2++}		
Oxy/Hydroxy	UOH^{+3} $UO_2(OH)_3^-$ $(UO2)3(OH)7$	$U(OH)_4(aq)$ $UO_2(OH)_4^{-2}$ $(UO2)3(OH)4+2$	UOH_2OH^+ $(UO_2)_2OH^{+3}$ $(UO_2)_3(OH)_5^+$	$UO_2(OH)_2(aq)$ $(UO_2)_2(OH)_2^{+2}$ $(UO_2)_4(OH)_7^+$
Carbonate	$U(CO_3)_4^{-4}$ $UO_2(CO_3)_3^{-4}$	$U(CO_3)_5^{-5}$ $UO_2(CO_3)_3^{-5}$	$UO_2CO_3(aq)$ $(UO_2)_3(CO_3)_6^{-6}$	$UO_2(CO_3)_2^{-2}$
Hydroxycarbonate	$(UO_2)_2CO_3(OH)_3$	$(UO_2)_3(OH)_5CO_2+$	$(UO_2)_3O(OH)_2(HCO_3)+$ $(UO_2)_{11}(CO_3)_6(OH)_{12}^{-2}$	
Nitrate/Azide	UNO_3^{+3} $UO_2(N_3)_2(aq)$	$U(NO_3)_2^{+2}$ $UO_2(N_3)_3^-$	$UO_2NO_3^+$ $UO_2(N_3)_4^{-2}$	$UO_2N_3^+$
Sulfate	USO_4^{+2}	$UO_2SO_4(aq)$	$UO_2(SO_4)_2^{-2}$	$U(OH)_2SO_4$
Sulfite/Thio	$UO_2SO_3(aq)$	$UO_2(SO_3)_2^{-2}$	$UO_2S_2O_3(aq)$	
Phosphate	$UO_2PO_4^-$ $UO_2(H_2PO_4)_2(aq)$	$UO_2H_2PO_4^+$ $UO_2(H_2PO_4)(H_3PO_4)^+$	$UO_2H_3PO_4^{+2}$	$UO_2HPO_4(aq)$
Fluoride	UF^{+3} UF_5^-	UF_2^{+2} UF_6^{-2}	UF^{3+}	$UF_4(aq)$
Oxyfluoride	UO_2F^+	$UO_2F_2(aq)$	$UO_2F_3^-$	$UO_2F_4^{-2}$
Chloride	UCl^{+3}			
Oxychloride	UO_2Cl^+	$UO_2Cl_2(aq)$	$UO_2ClO_3^+$	
Iodide/Iodate	UI^{+3}	$UO_2IO_3^+$	$UO_2(IO_3)_2(aq)$	
Bromide/Bromate	UBr^{+3}	UO_2Br^+	$UO_2BrO_3^+$	
SCN	$USCN^{+3}$ $UO_2(SCN)_2(aq)$	$U(SCN)_2^{+2}$	UO_2SCN^+	$UO_2(SCN)_3^-$
Organics	$U(Butanoate)^{+2}$ $U(Formate)2^+$	$U(Butanoate)_2^+$ $U(Propanoate)^{+2}$	$U(Pentanoate)^{+2}$ $U(Propanoate)_2^+$	$U(Formate)^{+2}$

Table 7 Groundwater compositions used in solubility speciation model

Constituent	Concentration (mg/1)	
	High Fluoride[1]	Low Fluoride [2]
Na^+	570	285
K^+	10	10
Ca^{+2}	10	10
Mg^{+2}	17	17
Fe^{+2}	1.61	
	0.01	
Al+3	0.7	0.001
$Zr(OH)_2^{+2}$	0.023	0.001
$SiO_2(aq)$	21	0.001
Cl^-	220	125
NO_3^-	7.8	300
HCO_3	763	294
SO_4^{-2}	350	61.4
F^-	20	0.36
TDS	1960	1103
pH	6.0,8.0	6.0,8.0
Eh	+200 to +700 mV	-300 to +700 mV

[1]From Fjeld, et al., 1998

[2]From Rodriguez, et a 1.,1997

Table 8 Plutonium solubility and controlling solid phase in three INEEL perched groundwater compositions

Redox (mV)	Low Fluoride, pH 8 Solubility	Phase	High Fluoride, pH 8 Solubility (M)	Phase	High Fluoride, pH 6 Solubility	Phase
700	1.9E-07	$PuO_2(OH)_2$	5.7E-06	$PuO_2(OH)_2$	4.9E-04	$Pu(OH)_4$
650	2.6E-07	$PuO_2(OH)_2$	5.8E-06	$PuO_2(OH)_2$	1.0E-05	$Pu(OH)_4$
630	1.6E-07	$Pu(OH)_4$	2.5E-06	$Pu(OH)_4$	2.2E-06	$Pu(OH)_4$
600	3.4E-08	$Pu(OH)_4$	2.7E-07	$Pu(OH)_4$	2.3E-07	$Pu(OH)_4$
550	5.5E-09	$Pu(OH)_4$	1.0E-08	$Pu(OH)_4$	9.6E-09	$Pu(OH)_4$
525	3.1E-09	$Pu(OH)_4$	3.9E-09	$Pu(OH)_4$	3.8E-09	$Pu(OH)_4$
500	2.3E-09	$Pu(OH)_4$	2.4E-09	$Pu(OH)_4$	2.4E-09	$Pu(OH)_4$
450	1.8E-09	$Pu(OH)_4$	1.8E-09	$Pu(OH)_4$	1.9E-09	$Pu(OH)_4$
400	1.8E-09	$Pu(OH)_4$	1.8E-09	$Pu(OH)_4$	1.8E-09	$Pu(OH)_4$
300	1.7E-09	$Pu(OH)_4$	1.7E-09	$Pu(OH)_4$	1.9E-09	$Pu(OH)_4$
250	1.7E-09	$Pu(OH)_4$	1.7E-09	$Pu(OH)_4$	2.4E-09	$Pu(OH)_4$
200	1.7E-09	$Pu(OH)_4$	1.7E-09	$Pu(OH)_4$	5.9E-09	$Pu(OH)_4$

Table 9 Plutonium speciation in low fluoride pH 8 groundwater

Eh (mV)	Stable Solid	Solubility (M)	$PuO_2(CO_3)_2^{2-}$ (%)	PuO_2^+ (%)	$Pu(OH)_4(aq)$ (%)	$PuO_2OH(aq)$ (%)
700	$PuO_2(OH)_2$	1.9E-07	93.43	6.46		
650	$PuO_2(OH)_2$	2.6E-07	66.69	32.33		
630	$Pu(OH)_4$	1.6E-07	47.63	50.29	1.10	
600	$Pu(OH)_4$	3.4E-08	21.29	72.26	5.07	1.36
550	$Pu(OH)_4$	5.5E-09	2.71	64.40	31.67	1.21
525	$Pu(OH)_4$	3.1E 09		42.80	55.70	0.80
500	$Pu(OH)_4$	2.3E-09		22.38	77.05	
450	$Pu(OH)_4$	1.7E-09		3.98	95.92	
400	$Pu(OH)_4$	1.7E-09			99.38	
350	$Pu(OH)_4$	1.7E-09			99.90	
300	$Pu(OH)_4$	1.7E-09			99.97	
250	$Pu(OH)_4$	1.7E-09			99.98	
200	$Pu(OH)_4$	1.7E-09			99.98	

Table 10 Plutonium speciation in high fluoride pH 8 groundwater

Eh (mV)	Stable Solid	Solubility (M)	PuO2F4-2 (%)	PuO2F3- (%)	PuO2(CO3) 2-2 (%)	PuO2+ (%)	Pu(OH)4(aq) (%)
700	PuO2(OH) 2	5.7E-06	46.29	44.47	8.54		
650	PuO2(OH) 2	5.8E-06	45.67	43.87	8.42	1.53	
630	Pu(OH)4	2.6E-06	44.82	43.06	8.27	3.26	
600	Pu(OH)4	2.7E-07	41.50	39.88	7.65	9.71	0.60
550	Pu(OH)4	1.0E-08	21.76	20.91	4.01	35.65	16.80
525	Pu(OH)4	3.9E-09	8.35	8.02	1.54	36.20	45.14
500	Pu(OH)4	2.4E-09	1.93	1.86		22.19	73.22
450	Pu(OH)4	1.8E-09				4.14	95.65
400	Pu(OH)4	1.8E-09					99.35
300	Pu(OH)4	1.7E-09					99.97
250	Pu(OH)4	1.7E-09					99.98
200	Pu(OH)4	1.7E-09					99.98

Table 12 Uranium solubility and controlling solid phase in two INEEL perched groundwater compositions

Redox (mV)	Low Fluoride, pH 8 Solubility(M)	Phase	High Fluoride, pH 6 Solubility (M)	Phase
800			1.0E-04	UO2CO3
700			1.0E-04	
650	1.3 E-04	CaUO4	1.0E-04	UO2CO3
600	1.3 E-04	CaUO4	1.0E-04	UO2CO3
500	1.3 E-04	CaUO4	1.0E-04	UO2CO3
400	1.3 E-04	CaUO4	1.0E-04	UO2CO3
300	1.1 E-04	CaUO4	1.0E-04	UO2CO3
200	1.1 E-04	CaUO4	1.1E-04	UO2CO3
100	1.1 E-04	CaUO4	3.4 E-08	Uraninite
0	2.6 E-06	Uraninite	4.1 E-10	Uraninite
-100	1.5E-09	Uraninite	3.9 E-10	Uraninite
-200	3.9E-10	Uraninite	7.9 E-04	Uraninite
-300	4.5E-10	Uraninite		

Table 13 Uranium speciation in low-fluoride pH 8 groundwater

Eh (mV)	Stable Solid	Solubility (M)	$UO_2(CO_3)_3^{-4}$ (%)	$UO_2(CO_3)_2^{-2}$ (%)	$(UO_2)_2CO_3(OH)_3^-$ (%)	$U(OH)_4(aq)$ (%)
650	CaUO4	1.3E-04	77.02	21.07	1.60	
600	CaUO4	1.3E-04	77.02	21.07	1.60	
500	CaUO4	1.3E-04	77.02	21.07	1.60	
400	CaUO4	1.3E-04	76.99	21.10	1.60	
300	CaUO4	1.1E-04	74.88	23.09	1.68	
200	CaUO4	1.1E-04	74.91	23.07	1.67	
100	CaUO4	1.1E-04	74.75	23.22	1.68	
0		2.6E-06	75.63	24.00		26.70
-100		1.5E-09	55.48	17.59		99.89
-200		3.9E-10				100.00
-300		4.5E-10				

Table 14 Uranium speciation in low-fluoride pH 6 groundwater

Eh (mV)	Stable Solid	Solubility (M)	$UO_2(CO_3)_2^{-2}$ (%)	$(UO_2)_2CO_3(OH)_3^-$ (%)	$UO_2CO_3(aq)$ (%)	$UO_2(OH)_2(aq)$ (%)	UO_2OH^+ (%)	$UO_2(CO_3)_3^{-4}$ (%)	$U(OH)_4(aq)$ (%)
800	UO_2CO_3	1.0E-04	29.08	51.50	15.84	2.50	0.36		
700	UO_2CO_3	1.0E-04	29.08	51.50	15.84	2.50	0.36		
600	UO_2CO_3	1.0E-04	29.08	51.50	15.84	2.50	0.36		
500	UO_2CO_3	1.0E-04	28.35	51.81	16.24	2.55	0.36		
400	UO_2CO_3	1.0E-04	28.35	51.81	16.24	2.55	0.36		
300	UO_2CO_3	1.0E-04	28.34	51.81	16.24	2.55	0.36		
200	UO_2CO_3	1.1E-04	31.91	49.98	14.33	2.31		0.72	
100	Uraninite	3.4E-08	36.81		27.96	4.40	0.66	1.47	1.15
0	Uraninite	4.1 E-10	2.23		0.98				96.43
-100	Uraninite	3.9E-10							100.00
-200	Uraninite	7.9E-04							100.00

APPENDIX H

Silica Flour Partitioning and Ceramic Cell Studies

Silica Flour Partitioning Study

The objective for conducting this partitioning study was to determine if the practice of using silica flour as a packing media for field lysimeters is appropriate for the collection of samples to measure the concentration of strontium and several actinides in groundwater and perched water below the subsurface disposal area at INEEL.

Distribution coefficients were experimentally determined for ^{85}Sr, ^{233}U, ^{241}Am, and ^{239}Pu(IV) in silica flour suspension concentrations of approximately 50,000 mg/L, 100,000 mg/L and 200,000 mg/L in the modified perched water simulant (MPWS). A known activity of each radionuclide was added to replicate 10-ml silica flour suspensions in 14-ml polycarbonate centrifuge tubes and equilibrated by rotating for a period of 10 days. Blank tubes were set for each radionuclide in replicate to determine the extent of sorption to the centrifuge tubes. After equilibration, each tube was centrifuged at 5000 rpm for 30 minutes using a Sorval RCB2 refrigerated centrifuge maintained at 22^{0}C ± 2^{0}C. Aqueous phase activity was measured by liquid scintillation and sorbed phase activity was calculated from a comparison of the initial activity and the aqueous phase activity for each of the replicate tubes.

Results of these experiments for each radionuclide are summarized in the attached table and include calculated distribution coefficients for each silica flour suspension concentration. Also included in the table are background corrected initial solution activity (C_0) and aqueous phase activity (C_{aq}) in units of CPM/ml. Distribution coefficients for ^{85}Sr and ^{233}U were 0.493 ± 0.178 and 2.45 ± 0.815 L/Kg respectively. These relatively low Kds suggest that silica flour does not significantly attenuate the mobility of neither strontium nor uranium, indicating that the use of silica flour as packing material for lysimeter cells is acceptable. However, the use of silica flour packing to measure groundwater concentrations of americium and plutonium may be problematic. Distribution coefficients for ^{241}Am and ^{239}Pu(IV) were experimentally measured at 448 ± 42 and 1764 ± 778 L/Kd respectively, suggesting that significant attenuation of these actinides is possible. It is important to note that these measured Kds (i.e. for Am and Pu) are likely confounded due to the chemical behavior of these actinides in the MPWS. Specifically, pH-E_H phase diagrams and speciation models predict the predominant solid species for the Am-C-O-H system to be Am(CO$_3$) and PuO$_2$ for the Pu-C-O-H system. Therefore, measured distribution coefficients for americium are likely a result of sorption onto the silica flour of the cationic species and precipitation of the carbonate solid. Speciation models such as EQ3/6 and Minteq are equilibrium models and most phase diagrams are developed based on thermodynamic equilibrium and even though the PuO$_2$ solid is predicted for the Pu-C-O-H system, it may not be present in significant amounts due to kinetic limitations. However, if the solid does not predominate, certainly hydrolyzed Pu species (Pu(OH)$^{3+}$, Pu(OH)$_2$$^{2+}$, Pu(OH)$_3$$^{1+}$ and Pu(OH)$_4$) do exist and the latter two species may

predominate at pH 8. Since each of the suspensions were incubated for a period of 10 days, it is possible that some PuO_2 solid was also formed. Therefore, the calculated Kd for plutonium is also confounded by the presence of hydrolyzed plutonium and the solid species.

This discussion to rationalize the behavior of americium and plutonium may be somewhat academic given the objective of the study. Regardless of the mechanism, be it sorption, precipitation of an Am species or formation of true Pu colloids, americium and plutonium are likely to be attenuated by silica flour. Attenuation by the silica flour would only be considered important if sorption of Am and Pu on the natural material surrounding the silica flour is less than sorption onto the silica flour.

Table H.1.   Distribution Coefficients (Kd's) for Sr, Am, Pu (IV), and U with silica flour

	Bkgd (CPM)		Co 364.9 Sr 7.5	Co 461 Am 0.15	Co 425.40 Pu (IV) 0.15	Co 4.10 Pu (V) 0.15	Co 570 U 0.15	
	Tube	SS (g/mL)	Aqueous Activity (CPM/mL) Gross Caq	Net Caq	Net Co/Caq	Kd (L/kg)	Cs (DPM/g)	Cs/Caq Kd
Sr	1	0.051040	361.4	353.9	1.01	0.194	69	0.193766
	2	0.057900	354.5	347	1.03	0.518	180	0.517637
	3	0.098880	346.5	339	1.05	0.549	186	0.548921
	4	0.102900	349.6	342.1	1.04	0.435	149	0.434633
	5	0.199050	319	311.5	1.15	0.740	231	0.740274
	6	0.202300	330.7	323.2	1.11	0.523	169	0.523069
	7	0	362	354.5				
	8	0	367.7	360.2				
Am	1	0.049650	20.3	20.15	22.87	440.503	8876	440.5029
	2	0.051060	19.8	19.65	23.45	439.736	8641	439.7361
	3	0.102460	10.5	10.35	44.53	424.815	4397	424.8152
	4	0.099200	9.4	9.25	49.82	492.153	4552	492.1534
	5	0.200610	6.0	5.85	78.78	387.706	2268	387.7064
	6	0.199570	4.7	4.55	101.29	502.509	2286	502.509
	7	0	342.9	342.75				
	8	0	329.9	329.75				
Pu (IV)	1	0.049000	9.9	9.75	43.62	869.702	8480	869.7017
	2	0.050850	9.5	9.35	45.48	874.755	8179	874.7548
	3	0.101190	2.9	2.75	154.64	1518.296	4175	1518.296
	4	0.100730	1.9	1.75	243.00	2402.462	4204	2402.462
	5	0.206380	1.0	0.85	500.29	2419.295	2056	2419.295
	6	0.199630	1.0	0.85	500.29	2501.098	2126	2501.098
	7	0	415.1	414.95				
	8	0	390.5	390.35				
U	1	0.059900	521.1	520.95	1.09	1.551	808	1.551038
	2	0.055400	526.6	526.45	1.08	1.471	774	1.470925
	3	0.102270	446.3	446.15	1.28	2.700	1205	2.700111
	4	0.099460	461.0	460.85	1.24	2.367	1091	2.367128
	5	0.201950	338.5	338.35	1.68	3.381	1144	3.380663
	6	0.203190	343.7	343.55	1.66	3.235	1111	3.234682
	7	0	568.2	568.05				
	8	0	580.0	579.85				

Ceramic Cell Study

Experiments were conducted to determine if the ceramic cells used in suction lysimeters significantly attenuated americium, plutonium, neptunium, or uranium as groundwater permeated the cells during a collection event. A ground water simulant was prepared for each of the actinides at approximately 0.033 µCi/ml in the modified perched water (MPWS) and transferred to a 250-ml beaker. A ceramic cell was placed in each solution for a period of five hours. The solution flowed into the cell through the ceramic material under the influence of gravity at approximately 0.067 ml/min for the first 2 hours and at 0.041 ml/min for the next 3 hours. Duplicate MPWS samples were collected at time zero and analyzed to determine the solution phase activity of each actinide. A second and third set of samples was collected at 2 and 5 hours analyzed as follows. After the initial 2 hours of exposure all of the solution in each cell was removed and analyzed as follows. A sample of the solution in each beaker (outside the cell) was collected and analyzed by liquid scintillation, filtered at 12 nm and reanalyzed. In addition, a sample of the solution inside the cell was collected and analyzed.

Calculations were made to determine if the actinides were attenuated as the MPWS flowed into the ceramic cell. Results are summarized in Table H-1 and the detailed data are presented in Table H-2. After 2 hours of contact 99.9 %, 81.9 %, 51.9 % and 6.6 % of Am, Pu, Np, and U, respectively, were retained by the ceramic material. After 3 additional hours of contact, 99.9 % and 89.4 % of the initial concentration of Am and Pu was removed from solution. Both Np and U also showed attenuation, but to a lesser extent. Attenuation of Np dropped from 51.9 % to 32.8% and the loss from solution for U dropped from 6.6 % to 2.7%.

Table H-2. Results of Ceramic Cell Study

Time Hr.	Percent Loss to Ceramic Cell			
	Am	Pu(IV)	Np	U
2	99.9	81.8	51.9	6.6
5	99.9	89.4	32.8	2.7

Table H-3. Detailed Data for Ceramic Cell Study

Time Hr.	Sample Type	CPU/mL			
		Am	Pu	Np	U
0	UF	790.6	717.8	700.0	894.1
0	UF	801.2	734.6	700.5	888.7
0	UF$_{AVG}$	795.9	726.2	700.25	891.4
2	UF	529.0	670.7	661.0	869.0
2	F	489.5	660.7	666.7	861.0
2	Cell	0.6	132.1	336.6	832.2
2	% particle in solution in beaker	7.5%	1.5%	0%	0.9%
2	% loss from original solution	33.5%	7.6%	5.6%	2.5%
2	% loss to cell	99.9%	81.8%	51.9%	6.6%
5	UF	311.3	651.9	667.1	854.2
5	F	275.9	650.2	648.4	877.9
5	Cell	0.5	77.2	470.7	867.1
5	% particle in solution in beaker	11.4%	0.2%	2.8%	0%
5	% loss from original solution	63.8%	10.2%	4.7%	4.1%
5	% loss to cell	99.9%	89.4%	32.8%	2.7%